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Recertification of the Standard Reference Material 1475A, A Linear Polyethylene Resin

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Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply necessarily the best available for the purpose.

ABSTRACT

Size exclusion chromatograms (SEC) and melt flow rate of SRM 1475a, a polyethylene resin, were determined and compared with measurements on samples of SRM 1475. Within the uncertainties of the measurements by SEC and melt flow rate, the measured characteristics of the SRM 1475a are identical to those of SRM 1475.

1.0 Introduction

This study was done to test the homogeneity of the material recently bottled called 1475a, and to compare SRM 1475a with material designated SRM 1475 which had been taken from the shelves of the Standard Reference Material Program (SRMP). This testing and comparison with SRM 1475 were done by using Size Exclusion Chromatography (SEC) and melt flow rate measurements.

2.0 Samples

2.1 Samples of SRM 1475

Four bottles of SRM 1475 were taken from the shelves of the current stock of SRM 1475. These materials were used to compare with bottles of SRM 1475a.

2.2 Preparation and Bottling of SRM 1475a

2.2.1 Preparation

The material for SRM 1475a and SRM 1475 is a linear polyethylene made by a single manufacturer in a single batch. Description of the material SRM 1475 is given in NBS Special Publication 260-42¹. The original bottling, the replacement bottling in 1986, and the current bottling were each taken from different 23 kg (50 lb) bags of the original production.

2.2.2 Bottling of SRM 1475a

A 23 kg (50 lb) bag of the polymer was given to SRMP for bottling. 448 samples were bottled in about 50 g sizes. The entire set of samples was divided into 15 subsets. One bottle was randomly selected from each subset for homogeneity testing. Testing was also done on the first and last bottles of the filling.

3.0 SEC of SRM 1475a and SRM 1475

SEC was performed on samples of SRM 1475 and SRM 1475a taken from all of the selected bottles, with duplicate samples taken from all four of the SRM 1475 bottles.

Earlier work on SRM 1475¹ indicated that the intrinsic viscosity of the material showed a pellet to pellet variation of as much as 8%. We are interested in studying this variation in the SEC. If we find any pellet to pellet variation by SEC, we wish to be able to distinguish the pellet to pellet variation from the bottle to bottle variation and to distinguish either of these variations from the difference between SRM 1475a, the new

stock, and SRM 1475, the old stock. We shall, in later sections, describe studies on solutions made up from single pellets and solutions made up of many pellets taken from both SRM 1475 and SRM 1475a.

3.1 Experimental Conditions

In this study a Waters 150-C ALC/GPC Liquid Chromatograph with a refractive index (RI) detector and a single Jordi Associates 50 cm long 10 mm ID mixed bed GPC column was used. The injector and column compartments were controlled at 137 °C. 1,2,4-trichlorobenzene (TCB) from Aldrich Chemical Company, with 0.01% Monsanto Santonox R added as a protective antioxidant, was used as the solvent. 0.3 g/L of octadecane (Eastman Kodak) was added to the solvent used to prepare solutions, as a SEC pump marker for all the following work.

The SRM 1475 and SRM 1475a samples were dissolved in the solvent at concentrations of approximately 1.0 g/L. Solutions were heated in an oven at 150 °C. Each bottle was shaken at frequent intervals to aid the dissolution of the polymer. Solutions were filtered at 150 °C through 5.0 µm pore size Millipore Mitex teflon membranes (Millipore LSWP 02500).

3.2 Methods of Comparison of Chromatograms

SEC chromatograms of samples of SRM 1475 and SRM 1475a were normalized to unit peak height and then compared by overlaying them to see if there were differences visually within the noise. We, also, compared chromatograms more quantitatively using a statistical technique called the match factor.

Several statistical techniques are available for comparison of chromatograms. For chromatograms containing only a small amount of fine structure, the correlation coefficient² of the signals from the two chromatograms gives a good idea of agreement between two chromatograms. This quantity of comparison, often called the match factor when comparing two chromatograms, is defined as³

$$\text{Match Factor} = 10^3 \left\{ \sum x * y - (\sum x * \sum y) / n \right\}^2 / \left[\left\{ \sum x^2 - \sum x * \sum x / n \right\} \left\{ \sum y^2 - \sum y * \sum y / n \right\} \right].$$

The values x and y are the measured signal in the first and second chromatogram, respectively, at the same time in the chromatogram; n is the number of data points. Sums are taken over all data points.

At the extremes, a match factor of 0 indicates no match and 1000 indicates identical chromatogram. Generally, values above 990 indicate that the chromatograms are similar. Values between 900 and 990 indicate there is some similarity, but the result

should be interpreted with care. All values below 900 mean, in effect, that the chromatograms are different.³

3.3 Results of SEC Studies

To estimate the effect of variation within the equipment a number of sets of multiple injections from the same solution have been studied. Visual comparison of one of these is seen in Fig. 1. Table 1 gives the match factors for two such sets. This indicates to us the optimum repeatability of a given experiment for these experimental conditions as reflected by the match factor. For these sets we see match factors in the range of 997 to 998.

In order to compare SRM 1475a with SRM 1475 without the pellet to pellet variation, 1.0 g/L solutions were made up of 24 to 30 pellets for each solution. Six pellets were taken from each of the four bottles of SRM 1475 for the solution used in SEC 6617. Six pellets were taken from each of four or five bottles of SRM 1475a for the four solutions used in SEC 6622 through SEC 6627. Again visual comparison of these solutions show the chromatograms are the same (Fig. 2). Match factors between these solutions are in the range 997 to 998 (table 2) showing SRM 1475 and SRM 1475a have chromatograms which are the same.

In Tables 3 to 5 we look at various aspects of the pellet to pellet variation. In Table 3 we see no pellet to pellet variation in one bottle of SRM 1475 from the agreement among the match factors. Bottle to bottle variation of SRM 1475 for a single pellet is seen in Table 4. The match factors indicate no detectable variation among single pellets from different bottles of the old stock of SRM 1475.

Table 5 shows the match factors for solutions of a single pellet from each sample bottle of SRM 1475a. The match factor is compared to the mixed pellet solution of SRM 1475. Again we see that all match factors are above 990.

3.4 Conclusions of SEC Studies

We find a small pellet to pellet variation in SRM 1475 from our SEC studies. Furthermore we find that there is no bottle to bottle variation in SRM 1475a. Finally, the chromatograms from SRM 1475 and SRM 1475a are found to be the same.

4.0 Melt Flow Rate of SRM 1475 and SRM 1475a

Melt flow rate as measured by ASTM D1238-90b⁴ is widely used in polymer technology as a product specification since this value, which includes a statement of the load and temperature under which it is obtained, gives an indication of the processing

properties of the polymer⁵⁻⁷. The value of melt flow rate is expressed as the mass of polymer melt pushed from the heated cylinder of the extrusion plastometer through its precision bore orifice by its piston in a period of time, the standard units of the value being grams per ten minutes (g/10 min).

4.1 Randomization of Charge Sequence of SRM 1475a

Three extrusions were made from each of the bottles of SRM 1475 and of SRM 1475a during the course of the melt flow rate experiments. The sequence of the extrusions was randomized according to a procedure described by Natrella⁸, using the Rand tables⁹.

4.2 Instrument Calibration and Alignment

4.2.1 Temperature Indication

The temperature was indicated by a mercury column thermometer of the form described in paragraph 5.7 of the ASTM method. Calibration of the temperature indication is traceable to the Thermometry Group of the NIST Process Measurements Division. A description of the calibration procedure is given in detail in NISTIR 4627¹⁰. The effect of an uncertainty in temperature on the melt flow rate of SRM 1475a is described in the subsequent section on uncertainty analysis.

4.2.2 Metering of Plastometer Components

The geometric dimensions of the cylinder, piston assembly, and dies were found to comply with the specifications described in the ASTM method.

The diameter of the cylinder bore was determined by a Brown and Sharpe model 599-281 Intrimik inner diameter (ID) micrometer. The ID of the bore was measured at the bottom end (micrometer head resting on a die at the bottom), and at levels from 15 cm down from the top end, up to 2 cm from the top end, in 1 cm intervals. All of the resulting measurements occurred in the range 0.95441 cm to 0.95504 cm, in compliance with the tolerance of this specification described in paragraph 5.2 of the ASTM method.

The apparent mass of the nominal 0.325 kg load was determined on an analytical balance with 1000 g capacity and 0.0001 g resolution. The apparent mass of the nominal 0.325 kg load was found to be 0.3250002 kg. well within the ± 0.5% tolerance described in paragraph 5.4.4 of the ASTM method.

4.2.3 Alignment of Plastometer

The cylindrical axis of the bore was aligned with the gravity vector by a plumb-line procedure described in detail in NISTIR 4627¹⁰. The deviation of the plumb bob pointer was observed to be less than 1 mm from the point which would indicate ideally vertical orientation of the cylinder bore, at the end of a pendulum length of 41 cm. Consequently, this procedure is considered to obtain alignment of the cylindrical axis of the cylinder bore with the gravity vector, with a calculated uncertainty of (1 mm/41 cm). Uncertainties cited in this report are considered equivalent to those corresponding to a 95% level of confidence, as explained in the subsequent section on uncertainty estimates in the melt flow rate data.

4.3 Melt Flow Rate of SRM 1475a and SRM 1475

The melt flow rates of SRM 1475a and SRM 1475 samples were determined by procedure A described in Section 9 of ASTM Method D-1238-90b⁴. Standard test condition 190/.325 was used. Thus the flow rate was determined at 190.0 ± 0.1 °C using a load of 0.325 kg. The flow rate of the melt was measured by a manually operated extrusion plastometer obtained from the Tinius-Olsen Testing Machine Co. The extrusions were conducted with a die of specially hardened steel supplied by the Stevens Testing Instrument Co. A 5.0 g charge of pellets was used for each extrusion. Note 14 of ASTM D1238-90b⁴ provides for the manual forcing of some resin out during the preheat period to eliminate bubbles in the test extrudate. This option was implemented by adding the 2.060 kg load weight to the top of the piston after a preheat of 4 minutes and 50 seconds to force out extra melt containing the last of the bubbles, and then withdrawing the extra load from the piston at the moment the lower scribe mark of the 4 mm start section of the piston is approximately 1 mm above the guide collar. It was observed that this temporary extra load was always withdrawn during the interval between 5 minutes and 30 seconds and 5 minutes and 40 seconds of preheat. The end of the 6 minutes preheat period was marked as the beginning of timed test extrusion by making the initial extrudate cut at 6 minutes and discarding the preheat segment. It was also observed that the 4 mm start section of the piston had always entered the top of the guide collar part way at the moment of the initial cut to begin collecting timed test extrudate. Three timed test extrudate segments were cut at 3 minute intervals thereafter. After the third timed test extrudate segment had been cut, the remaining melt in the cylinder was purged and discarded.

The piston, die, and bore were cleaned free of the polymer at the end of each extrusion. Tools of brass and copper, considerably less hard than steel, were applied in the cleaning

process. The use of steel tools was avoided in order to prevent changing dimensions of instrument components due to cleaning wear.

In the earlier extrusions of SRM 1475, conducted without any procedural modifications during preheat, the first timed test extrudate generally contained some bubbles immediately following preheat¹¹⁻¹². In the present study fifteen extrusions were also conducted on 3.8 g charges of SRM 1475a without the procedural modification during preheat described above. The resulting early timed test extrudate contained some bubbles. However, there appeared to be no statistically significant difference between the two sets of results from the different procedures, despite the presence of bubbles in the early timed test extrudates from the unmodified procedure. The melt flow rate measured for these early extrusions was 2.01 g/10 min with a standard deviation of 0.032 g/10 min. The melt flow rate measured for SRM 1475a, with the procedure modified to purge all bubbles in the preheat extrudate by temporarily adding an extra load, is 2.02 g/10 min with a standard deviation of 0.026 g/10 min. The value of 2.01 g/10 min for the early procedure is well within the standard deviation of the above value.

4.4 Data Analysis on SRM 1475 and SRM 1475a

Data from 69 charges (57 charges SRM 1475a, 12 charges SRM 1475) were analyzed for the 0.325 kg load following the ASTM Method D1238-90b. The average melt flow rate of SRM 1475a was found to be 2.02 g/10 min with a standard deviation of a single measurement of 0.026 g/10 min. This standard deviation includes bottle to bottle, charge to charge, and day to day variability. The standard deviation of the mean was calculated to be 0.0036 g/10 min. Our estimates of systematic uncertainties in the measurement will be discussed in the following sections.

The melt flow rate of the SRM 1475 measured in this current series is 2.01 g/10 min with a standard deviation of a single measurement of 0.025 g/10 min. Clearly the melt flow rate of the SRM 1475 from the SRMP stock is indistinguishable from that of the newly bottled SRM 1475a.

4.5 Uncertainty Estimates of Melt Flow Rate Data

The NIST policy on reporting uncertainties in measurement¹⁴ requires that reported uncertainties be equivalent to the level of two standard deviations. The uncertainties cited in the following sections must ultimately be combined with the reproducibility uncertainty derived from the precision limits tabulated also at the 95% level of confidence in the ASTM method⁴. Consequently, the uncertainties cited in this report

are considered equivalent to those corresponding to a 95% level of confidence.

4.5.1 Repeatability and Sampling Uncertainties

In this section we discuss the uncertainty in terms of variations of the measured melt flow rate arising from sampling and bottling differences.

The overall repeatability is computed for a 95% confidence interval in an effort to maintain consistency with the practice implied in ASTM D 1238-90b which tabulates 95% confidence interval estimates. This was accomplished by applying a coverage factor of 2 to the standard deviation of the mean, 0.0036 g/10 min., to obtain the expanded uncertainty, $U = 0.0072 \text{ g}/10 \text{ min.}$, in compliance with the NIST policy governing the reporting of uncertainties in measurement¹⁴. This result gives an uncertainty of 0.36% due to overall repeatability, at a 95% level of confidence.

4.5.2 Charge to Charge Variability Within a Bottle

As described in Section 2.2, 17 bottles were selected for measurement from the original bottling. Two of these characterization bottles were selected for a study of charge to charge variation within a bottle. Melt flow rate determinations were conducted on six charges of polyethylene from each of these two bottles.

4.5.3 Bottle to Bottle Variability

In addition to the charges taken from the two bottles described in Section 4.5.2 above, melt flow rate determinations were also conducted on three charges taken from each of the other 15 bottles. The bottle to bottle variability was estimated from the population of all charges taken from all 17 bottles. The mean value of the melt flow rate for any bottle was found to lie within two standard deviations of the mean value of the melt flow rate for all the charges.

4.5.4 Day to Day Variability

Eight melt flow rate experiments could be done in a single day. The plastometer was occasionally shut down for a few days before the next set of extrusions was conducted. With this procedure we hoped to show the effects of day to day variability on the equipment and have that reflected in our standard deviation. However in general the day to day variability was small compared to the charge to charge variability.

4.5.5 Systematic Uncertainties

Obtaining a systematic uncertainty analysis of the melt flow rate is a difficult matter since the melt flow rate is not a fundamental property of the material and there is no simple relationship describing its estimation. Nonetheless we shall make an effort in this section to estimate the possible causes of uncertainty and their contribution to the overall actual uncertainty in the measurement made.

4.5.5.1 Instrument Variability

As noted before, the estimates of our own repeatability are in Table 6. These data reflect the repeatability of our own experiments and do not reflect any instrument-to-instrument or operator-to-operator variation since we had only one of each.

However, Table 5 in ASTM D1238-90b provides a means of estimating the uncertainty among a large population of instruments and operators applying procedure A. Their tabulated results include the average flow rate of a polyethylene under condition 190/2.16 of 2.04 g/10 min resulting from determinations by procedure A at nine laboratories. The standard deviation of this average is ± 0.079 g/10 min. from which they compute a reproducibility within ± 0.224 g/10 min, or $\pm 11\%$ of the mean. The reproducibilities listed in the ASTM tables are 95% confidence interval limits. Since the melt flow rate of this polyethylene used in the ASTM interlaboratory study is closely comparable with the melt flow rate determined for SRM 1475a, the results in Table 5 of the ASTM method provide an estimate for the reproducibility of the certificate melt flow rate of SRM 1475a within 2.02 ± 0.22 g/10 min in 95% of the results from a large population of laboratories using different instruments and different operators. This uncertainty due to instrument and operator variability is also given in Table 6 of this report.

4.5.5.2 Measurement Uncertainties

An effort is made to estimate the intrinsic uncertainty in the measurement. We do this by considering the uncertainties in the measured quantities (mass and time) as well as the uncertainties in the controlled quantities (temperature and the specifications on the instrument). The melt flow rate, F , is given by

$$F = \text{Mass}/\text{Time}$$

Thus the relative uncertainty in the melt flow rate, U_F/F , is then obtained as the root-sum-of-squares of the uncertainties in the systematic physical factors upon which the melt flow rate depends¹⁴

$$(U_F/F)^2 = (U_m/m)^2 + (U_t/t)^2 + (c_T U_T/T)^2.$$

The fractional uncertainty in weight of extrudate, U_m/m , is taken to include uncertainty in mass indication by the balance and to moisture pickup by the extrudate, and also to uncertainty in extrudate mass attending the cutting process. U_t/t is the fractional uncertainty in timing of the extra date cut, i.e. uncertainty in time indication by the stopwatch. The U_T/T term arises from the uncertainty in the temperature control and in the calibration of temperature indication. The factor c_T is the sensitivity coefficient defined in Ref. 15, $c_i \equiv (\partial f / \partial x_i)$. In the present context $c_T = (\partial F / \partial T)$ is the sensitivity of the apparent flow rate to small changes in melt temperature. The causes of these uncertainties are discussed in the next few paragraphs. These with the other uncertainties are given in Table 6 as well as an estimate of the combined expanded uncertainty resulting from all sources.

4.5.5.2.1 Weighing Uncertainty

The extrudate segments were weighed on a balance with 0.01 mg resolution and an estimated uncertainty of 0.05 mg. Replicate weighings of the segments always agreed to within ± 0.05 mg. Paragraph 9.9 of ASTM Method D 1238-90b instructs the experimenter to "weigh the extrudate to the nearest 1 mg when cool."

The extrudate segments were routinely weighed within one hour after having been cut, in compliance with the instruction in paragraph 9.9 of the ASTM method. Considering the hydrophobic character of polyethylene it would not be anticipated that the extrudate would accumulate moisture beyond the initial cooling stage prior to being weighed. On a few occasions during the characterization of another polyolefin, extrudate segments, which had been weighed at the end of a day, were weighed again on the following day without detecting any statistically valid change of weight within the groups. All individual changes, either positive or negative, were much smaller than 0.1 mg.

The extrudate weight was about 600 mg. The overall weighing uncertainty from the above sources is 0.15 mg with a minimum 95% level of confidence. Then the relative uncertainty

$$U_m/m = 0.03\%.$$

We take the uncertainty in the weighing as zero.

4.5.5.2.2 Timing Uncertainty

The interval (t) between extrudate cuts for SRM 1475a was measured with a battery powered stopwatch having a 0.01 s resolution in time indication and an uncertainty of less than 0.05 s. Thus the extrudate cut was assumed to be timed to better than 0.1 s. Consequently we take 0.1 s as a practical estimate of the timing uncertainty. Hence, the relative uncertainty in time interval may be expressed

$$U_t/t = \pm 0.1 \text{ s}/180 \text{ s} = 0.06\%$$

We take the timing uncertainty as zero.

4.5.5.2.3 Temperature Uncertainty

As described in section 4.2.1, the extrusion temperature was indicated by a mercury column thermometer of the form described in paragraph 5.7 of the ASTM method. The uncertainty of the thermometer is certified to be within the tolerances of the ASTM method, by comparison to standards traceable to NIST. The uncertainty in the temperature indication calibration is less than 0.1 °C.

Paragraph 5.7 in the ASTM method acknowledges that the temperature in the thermometer well may not necessarily be the temperature of the polymer melt at the calibration point in the bore. This is due to the steady state heat transfer gradients in the plastometer cylinder. Thus, the thermal profile of an undisturbed column of polyethylene melt was scanned along the cylindrical axis of the cylinder bore while the temperature was maintained at 190.0 °C at the calibration point in the melt column. This experiment was conducted in another extrusion plastometer during an earlier determination of the melt flow rate of SRM 1475. The column of melt was held stationary by plugging the flow. The temperature in the stationary melt column was measured with a thermocouple hot junction stationed at different heights above the top surface of the die, along the cylindrical axis of the bore. Throughout the experiment the reading of the mercury column thermometer remained at 190.0 ± 0.1 °C. The results are listed in Table 7.

Inspection of the tabulated results indicates that the departure of melt temperature from the indicated cylinder temperature is within ± 0.1 °C at any location in the melt column from 12 mm above the die upward. There is a 0.7 °C drop in temperature between the 12 mm and 1 mm levels above the die. This temperature drop is probably at least partially erased by the downward flow of melt during an extrusion. Since we have no other measurements on this profile, we may suppose another column may have a different profile. Thus, we estimate the contribution to the uncertainty from the temperature profile to be 0.7 °C.

Thus we assume a total temperature uncertainty of 0.8 °C, from temperature indication and from profile effects.

The effect of temperature variation on the melt flow rate of SRM 1475a was determined by conducting a set of three extrusions at 188.2 °C and another set of three extrusions at 191.6 °C. The two sets of three extrusions at the different temperatures were conducted with charges all taken from the same bottle of polyethylene resin. The results are listed in Table 8.

Linear regression analysis of melt flow rate versus temperature provided an equation with the slope, 0.018 g/10 min per °C. The slope, dF/dT , is taken as the sensitivity coefficient, c_T , of the flow rate to variation in temperature of the melt.

Considering the nominal temperature uncertainty, $U_T = 0.8$ °C, this result affords an estimate of ± 0.014 g/10 min for the uncertainty in melt flow rate of SRM 1475a due to uncertainty in temperature. The relative uncertainty in melt flow rate due to uncertainty in temperature is then $0.014/2.02$, or 0.7%.

4.6 Comparison with Earlier Melt Flow Measurements

As discussed in section 2.2.1, the material for SRM 1475a and SRM 1475 is a linear polyethylene made by a single manufacturer in a single batch. The original bottling, the replacement bottling in 1986, and the current bottling were each taken from different 23 Kg (50 lb) bags of the original production. Melt flow rate measurements were made on samples after each bottling.

The 1968 bottling gave a melt flow rate of 2.07 g/10 min with a standard deviation of 0.040 g/10 min and 41 degrees of freedom, that in 1986 gave a melt flow of 1.98 g/10 min with a standard deviation of 0.031 g/10 min and 29 degrees of freedom, and the current measurement gave 2.02 g/10 min with a standard deviation of 0.026 g/10 min and 56 degrees of freedom. An F test at the 5% level on the above melt flow averages suggests that the averages of the melt flow rates measured in 1968, 1986 and 1992 are indeed statistically different.

There may be a number of causes for the above difference. In the next few paragraphs we shall review these possibilities.

First there may have been differences in the materials themselves. As we pointed out earlier in the report, the materials for SRM 1475 and SRM 1475a came from one batch of polymer made for the original 1968 certification of SRM 1475. This material came in 23 Kg bags. There may have been a bag to

bag variability of the original material. As far as we are aware this is not studied directly in the original certification. However a modification of a bag-to-bag study is described in the 1968 paper.¹ "Forty-two samples for melt flow rate determination were taken from 13 different regions in seven of the bags. The standard deviation for samples within a region was found to be 2.1 percent, based on 29 degrees of freedom. The standard deviation between regions was found to be 1.7 percent, based on 12 degrees of freedom". From this statement we may imply no bag-to-bag variability was seen in the 1968 work. Furthermore, SRM 1475 and SRM 1475a were taken from different bags. The data from the SEC and the melt flow rate in the current work on SRM 1475 and SRM 1475a does not suggest a bag to bag variability.

The material could have changed over these 20 or so years. However, the melt flow rate measurements certainly do not follow a monotonic drift in time so degradation of a property like molecular weight seems unlikely.

Second, these small differences in melt flow rate determination could have arisen from instrumental variations over the period of 25 years. Although our instrument meets all ASTM D1238 specifications, instrumental variations uncontrolled by the method may be causing this difference. For example, in earlier studies we have looked at how the melt flow is changed as a result of changes in the piston foot and found these to be minimal. However, others have found that the rounding of the edge of the foot causes changes in the measured melt flow.¹³ Furthermore, the original melt flow characterization was conducted with a plastometer cylinder different from that used in the two subsequent characterizations. Differences in the thermal gradient in the cylinders may cause changes in the melt flow rate.

Third, changes in the melt flow rate methodology may cause changes in the melt flow rate measurements. For example, following the instrument manufacturer's instructions, the plastometer cylinder bore was cleaned with the aid of Hodag Antifoam F-1 solvent during the 1968 characterization of SRM 1475. Cleaning the bore has been performed without using any solvent during melt flow rate determinations since that time. Also, although a suitable silicone fluid was recommended as one possible fluid to enhance thermal conductivity in the thermometer well of the plastometer cylinder, in earlier editions of D1238 (see Note 7 in ASTM D1238-82), more recent editions of the method (e.g. Note 8 in ASTM D1238-88) instruct the reader that "Silicone oil, as a heat transfer medium should be avoided...". In fact it had been observed during an earlier characterization of another polyolefin, during the interval in which a silicone oil was used as a thermal conductivity enhancing fluid in the thermometer well, that the first extrusion of each day was slightly higher

than the average melt index for the extrusions which followed. It is now hypothesized that silicone oil vapor from the thermometer well may have been condensing inside the cylinder bore overnight with an accumulation adequate to slightly lubricate the bore before adding the first charge of the morning, and that the first charge and subsequent bore cleaning was adequate to cleanse the bore free of any trace of the silicone oil.

Finally, as discussed in section 4.5.5.1, there is a laboratory to laboratory variation of about 11% in this range of measurement found in round robin work on polyethylene with ASTM D1238. All of the above possible uncertainties may well be included in this 11%. Certainly the maximum difference of less than 5% between melt flow rate measurements made over a 24 year period of is well within this uncertainty.

4.7 Combined Expanded Uncertainty

The combined expanded uncertainty¹⁴ for the melt flow rate, U_c , is obtained as the root-sum-of-squares of component uncertainties from all sources, including the uncertainty due to reproducibility. The resulting initially calculated $U_c=11.03\%$ is not really distinguishable from the uncertainty due to reproducibility, 11%, which is predicated on results tabulated by the ASTM from nine laboratories. Therefore the combined expanded uncertainty is rounded up to 12% to include uncertainty from the reproducibility plus the uncertainties from all other sources, the result being significantly greater than the uncertainty due to reproducibility alone.

4.8 Conclusions of Melt Flow Rate Study

The melt flow rate of SRM 1475a was found to be 2.02 g/10 min, with a standard deviation of an average single measurement of 0.026 g/10 min, in close agreement with the currently measured value of 2.01 g/10 min, with a standard deviation of 0.025 g/10 min, for SRM 1475. The combined expanded uncertainty for the melt rate of SRM 1475a is 12%, or 0.24 g/10 min.

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13. Private Communication, George J. Ouellette, Jr., Himont Research and Development Center, Wilmington, DE.
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Table 1

Comparison of Chromatograms with Multiple Injections From a Single SEC Vial.

SEC Vial #1

SEC Run # Match Factor

6626 vs 6625	998.0
6627 vs 6625	997.9
6628 vs 6625	998.0

SEC Vial #2

SEC Run #

6620 vs 6619	997.6
6621 vs 6619	997.7
6622 vs 6619	997.5

Table 2

Match factor to compare chromatograms of solution of SRM 1475 with solution of SRM 1475a. Each solution is made up of 24 to 30 pellets, 6 from each of 4 or 5 bottles of SRM 1475 or SRM 1475a.

<u>Pellets from Bottles#</u>	<u>SEC Run #</u>	<u>Match Factor</u>
SRM 1475 1, 2, 3, 4	6517	
SRM 1475a 1, 2, 58, 62	6522 vs 6517	997.9
SRM 1475a 97, 145, 172, 208	6523 vs 6517	997.7
SRM 1475a 219, 258, 291, 322	6524 vs 6517	997.7
SRM 1475a 337, 377, 391, 435, last	6625 vs 6617	997.7

Table 3

Pellet to Pellet Variation Within a Single Bottle.

Each solution is made up from a single pellet of SRM 1475, bottle #3 old stock.

SEC Run #	Match factor
6605 vs 6604	992.9
6606 vs 6604	994.7
6607 vs 6604	995.1
6588 vs 6587	990.0
6590 vs 6587	991.0
6591 vs 6587	991.9

Each solution from a single pellet of SRM 1475a from bottle 322, new stock.

SEC Run #	Match factor
6672 va 6671	997.4
6673 vs 6671	997.1
6674 vs 6671	996.2
6675 vs 6671	997.2

Table 4

Comparison of Different Bottles of SRM 1475. Each of the four solutions is made up of one pellet. Each pellet comes from a different bottle of old stock SRM 1475.

SRM 1475 Bottle #	SEC Run #	Match Factor
1	6600	
2	6601 vs 6600	995.9
3	6602 vs 6600	997.8
4	6603 vs 6600	997.7

Table 5

Each solution is made from 1 pellet. Each pellet comes from a different bottle of SRM 1475a. These solutions are compared to the mixed pellet solution of SRM 1475.

SRM 1475a Bottle #	SEC Run #	Match Factor
1	6609 vs 6617	995.2
2	6610 vs 6617	997.4
58	6611 vs 6617	997.8
62	6612 vs 6617	997.9
172	6613 vs 6617	997.6
97	6614 vs 6617	997.9
145	6615 vs 6617	998.1
208	6616 vs 6617	996.6
377	6629 vs 6617	997.6
394	6630 vs 6617	993.5
435	6631 vs 6617	997.8
337	6632 vs 6617	997.7
219	6633 vs 6617	996.2
258	6634 vs 6617	996.2
291	6635 vs 6617	993.2
322	6636 vs 6617	992.8
last	6637 vs 6617	997.9

Table 6

Estimates of Uncertainties in Melt Flow Rate of SRM 1475a
Polyethylene Under Condition 190/0.325

1. Uncertainty due to repeatability of experiment	0.36%
2. Uncertainty due to Instrument Variability as estimated from reproducibility reported in ASTM method	11%
3. $U_m/m \times 100$	0.0%
4. $U_t/t \times 100$	0.0%
5. $U_T/T \times C_T^a$	0.7%
6. Combined expanded uncertainty, U_c^b	12%
a. Sensitivity coefficient, $C_T = dF/dT$, for variation of flow rate in response to small changes in melt temperature.	
b. The combined expanded uncertainty computed by root-sum-of-squares of the component uncertainties was only 11.03%, not statistically distinguishable from the component uncertainty due to reproducibility alone, 11%, considering the uncertainty in reproducibility itself. The combined expanded uncertainty is rounded up to $U_c=12\%$.	

Table 7

Variation of Temperature with Height in
Undisturbed Melt in Cylinder Bore

Height Above Die, mm	Melt Temp. Degrees C
48	190.09
36	189.93
24	189.97
12	189.94
1	189.23

Table 8

Temperature Dependence of the Melt Flow Rate (F) of
SRM 1475a in the Vicinity of 190 °C Under 0.325 Kg Load

<u>Temp. °C</u>	<u>F-T/0.325, g/10 min.</u>
188.2	2.000
190	2.020
191.6	2.061
$(dF/dT) = 0.018 \text{ g/10 min. per degree}$ $u = \pm 0.008 \text{ g/10 min. per degree}$	

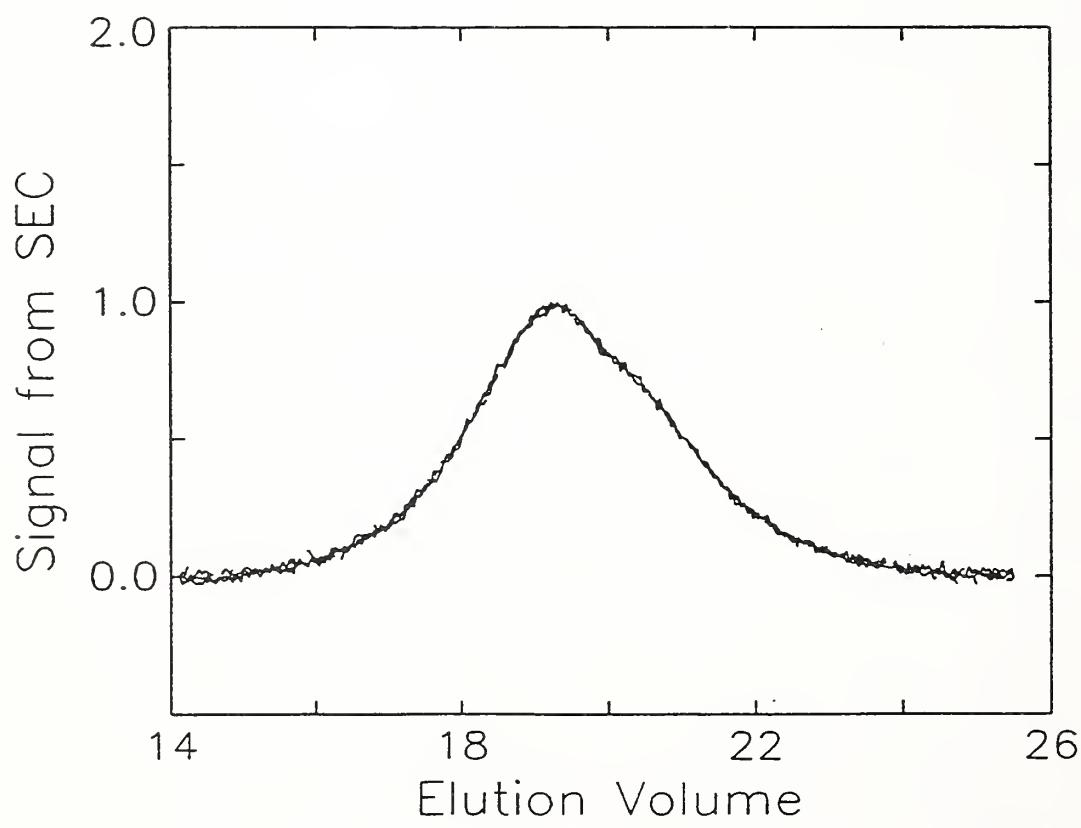


Figure 1 Overlay of SEC chromatograms from SEC run numbers 6619 to 6622 showing repeatability of injection.

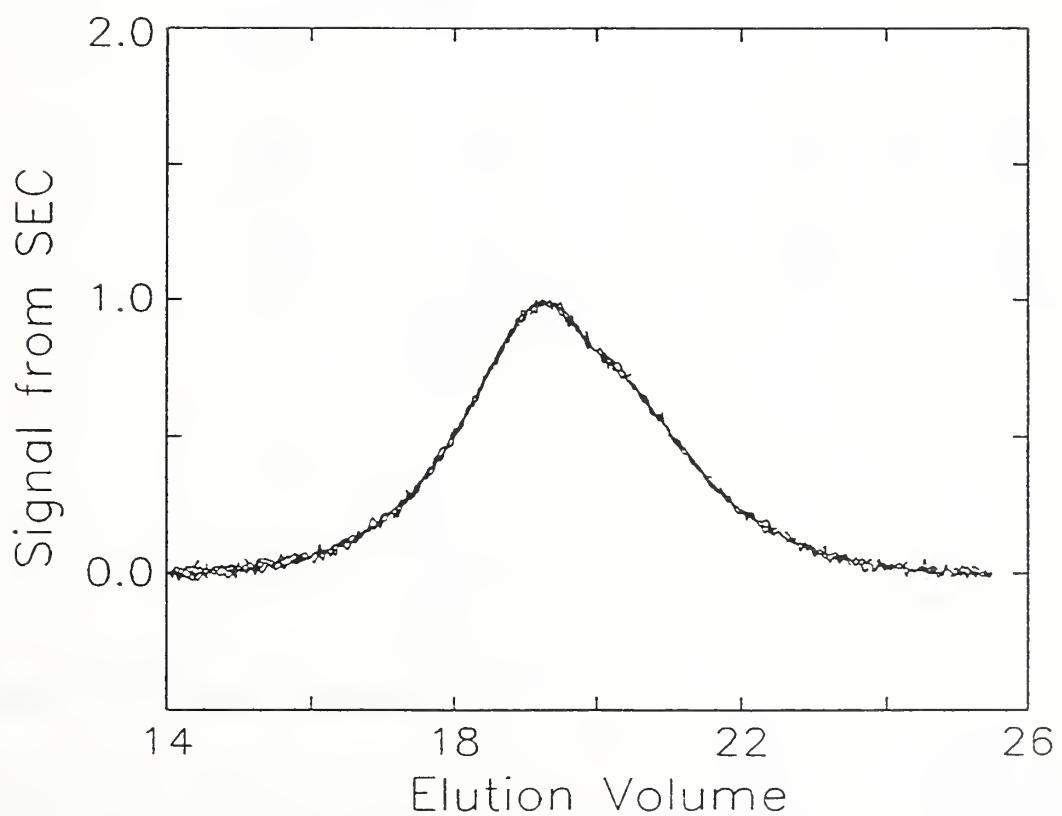


Figure 2 Overlay of SEC chromatograms from SEC run numbers 6617 and 6622 to 6625 comparing chromatograms of SRM 1475 with those of SRM 1475a.



National Institute of Standards & Technology

Certificate

Standard Reference Material 1475a

Linear Polyethylene

(Whole Polymer)

This Standard Reference Material (SRM) is intended for the calibration and evaluation of instruments used in polymer technology and science for the determination of molecular weight and molecular weight distribution and for use as a characterized sample for measurements of other physical properties of linear polyethylene. This SRM is supplied as pellets of polyethylene in a 50 g unit.

<u>Property</u>	<u>Certified Value*</u>		
Melt-Flow Rate ^a , g/10 min	2.02	±	0.24 ^a
Molecular Weights, g/mol:			
Weight-average molecular weight ^b	52,000	±	2,000
Number-average molecular weight ^c	18,310	±	360
Weight-average molecular weight ^c	53,070	±	620
Z-average molecular weight ^c	138,000	±	3,700
Ratio of molecular weight M _z :M _w :M _n ^c	7.54:2.90:1		
Molecular weight distribution ^c	(See Table 1)		
Limiting Viscosity Numbers ^d , mL/g:			
at 130 °C in 1-chloronaphthalene	89.0	±	0.32
at 130 °C in 1,2,4-trichlorobenzene	101.0	±	0.86
at 130 °C in decahydronaphthalene ^e	118.0	±	0.32
Solid Density ^f , g/cm ³	0.97844	±	0.00004
Heat Capacity	(See Table 2)		

*Melt-Flow Rate uncertainty parameters are described in Table 3. All other uncertainties are expressed as the standard deviation of the mean.

^aBy procedure A, ASTM Method D1238-90b, Test Condition 190/0.325.

^bBy light scattering in 1-chloronaphthalene at 135 °C.

^cBy size exclusion chromatography.

^dSample must be of adequate size. See directions for use on page 3.

^e"Technical" grade, which assayed at approximately equal proportions of cis- and trans-decahydronaphthalenes.

^fBy ASTM Method D1505-67; sample prepared by procedure A, ASTM Method D1928-68.

Gaithersburg, MD 20899

December 28, 1993

(Revision of certificate dated 7-1-93)

Thomas E. Gills, Acting Chief
Standard Reference Materials Program

Original certification of SRM 1475 was performed in the NIST Polymers Division by C.A.J. Hoeve, H.L. Wagner, J.E. Brown, A.B. Bestul, S.S. Chang, R.G. Christensen, L.J. Frolen, J.R. Maurey, G.S. Ross, and P.H. Verdier. Measurements comparing SRM 1475a to SRM 1475 were performed by C.M. Guttman and J.R. Maurey of the NIST Polymers Division.

The technical and support aspects involved in the revision, update, and issuance of this SRM were coordinated through the Standard Reference Materials Program by J.C. Colbert.

NOTICE AND WARNING TO USERS

Expiration of Certification: This certification is valid for five years from date of shipment from NIST.

Storage: SRM 1475a should be stored in its original bottle, tightly closed, and under normal laboratory conditions.

Table 1. Cumulative Molecular Weight Distribution by Gel-Permeation Chromatography

<u>Log M</u>	<u>Wt %</u>	<u>Log M</u>	<u>Wt %</u>	<u>Log M</u>	<u>Wt %</u>
2.800	0.0	4.014	15.2	5.065	90.7
2.865	0.005	4.070	18.1	5.113	92.2
2.929	0.020	4.126	21.5	5.161	93.7
2.992	0.052	4.182	25.2	5.209	94.8
3.056	0.105	4.237	29.3	5.256	95.8
3.119	0.185	4.292	33.7	5.303	96.6
3.181	0.343	4.346	38.5	5.349	97.3
3.243	0.475	4.400	43.4	5.395	97.9
3.305	0.706	4.454	48.5	5.440	98.4
3.366	0.999	4.507	53.5	5.485	98.7
3.427	1.38	4.560	58.3	5.530	99.1
3.488	1.88	4.612	62.9	5.574	99.3
3.548	2.51	4.664	67.3	5.618	99.5
3.607	3.30	4.715	71.4	5.662	99.7
3.667	4.28	4.766	75.1	5.705	99.8
3.725	5.46	4.817	78.5	5.789	99.9
3.784	6.87	4.868	81.6	5.87	100.0
3.842	8.56	4.918	84.4		
3.900	10.50	4.967	86.7		
3.957	12.7	5.016	88.9		

MATERIAL SOURCE AND PREPARATION

This sample of linear polyethylene was obtained from E.I. duPont de Nemours and Company of Wilmington, DE. It has an ash content of 0.002%. No volatiles were detected by a gas-chromatographic procedure capable of detecting 0.5% volatiles. The manufacturer added 111 mg/kg of the antioxidant, Irganox 1010 (Ciba-Geigy), which is tetrakis [methylene-3-(3',5'-di-t-butyl-4'-hydroxyphenyl)propionate]methane.

The size exclusion chromatograph was calibrated with linear polyethylene fractions obtained by a column elution technique. These fractions were characterized for use in the calibration procedure by determining their weight-average molecular weights by light-scattering, and their number-average molecular weights by membrane osmometry.

Directions for Use: A pellet-to-pellet coefficient of variation of 3% in the limiting viscosity number was found. All determinations should be performed on samples containing at least 50 pellets or 1 g of polymer (or material from a 1 g homogeneous blend). This will reduce the expectation of the standard error due to pellet variability to less than 0.5%.

For determination of melt flow rate by automated procedure B in the ASTM Method, the melt density can be found in Table 4 of ASTM D1238-90b.

Heat Capacity: Heat capacities $C_p(\rho, T)$ at various temperatures are given at two 23 °C densities, $\rho = 0.954$ and $\rho = 1.000 \text{ g/cm}^3$ in Table 2. These density values differ from the certified density value in this certificate. [2,3]

At densities between 0.954 and 1.000 g/cm^3 , obtained by varying the thermal history and crystallization conditions, the heat capacity is given by:

$$C_p(\rho, T) = C_p(1.000, T) + \frac{1-\rho}{0.17\rho} \Delta C(T),$$

where $\Delta C(T)$ is also tabulated in Table 2. These values may be used to check the values obtained with dynamic thermal analysis instruments when the heating rate approaches zero.

Errors in calculated $C_p(\rho, T)$ are believed to be less than 1% between 25 and 360 K and increase to about 5% at 5 K.

Table 2. Heat Capacity per Mole (14.027 g) of [-CH₂-]

T K	C _p (0.954,T)	C _p (1.000,T) J/(mol•K)	ΔC(T)
5	0.024	0.014	0.038
10	0.173	0.106	0.235
15	0.473	0.342	0.458
20	0.904	0.727	0.619
25	1.433	1.231	0.706
30	2.027	1.819	0.728
35	2.664	2.465	0.702
40	3.322	3.135	0.652
45	3.981	3.811	0.587
50	4.626	4.475	0.516
60	5.841	5.730	0.385
70	6.935	6.855	0.288
80	7.911	7.847	0.230
90	8.786	8.725	0.208
100	9.579	9.511	0.226
110	10.31	10.23	0.30
120	11.01	10.88	0.47
130	11.70	11.49	0.78
140	12.44	12.07	1.31
150	13.18	12.62	1.98
160	13.91	13.17	2.61
170	14.61	13.73	3.15
180	15.30	14.30	3.59
190	15.98	14.87	3.94
200	16.66	15.47	4.25
210	17.36	16.08	4.58
220	18.10	16.70	5.00
230	18.91	17.35	5.55
240	19.80	18.03	6.29
250	20.76	18.72	7.22
260	21.76	19.45	8.19
270	22.78	20.23	9.06
280	23.80	21.04	9.81
290	24.83	21.89	10.47
300	25.87	22.76	11.09
310	26.95	23.64	11.80
320	28.11	24.54	12.72
330	29.39	25.46	13.97
340	30.86	26.46	15.63
350	32.59	27.57	17.76
360	34.65	28.90	20.31
273.15	23.10	20.48	9.31
298.15	25.68	22.60	10.93

Table 3

Estimates of Uncertainties in Melt Flow Rate of SRM 1475a
Polyethylene Under Condition 190/0.325 [4,5]

1. Uncertainty due to repeatability of experiment	0.36%
2. Uncertainty due to instrument variability as estimated from reproducibility reported in ASTM method	11%
3. Uncertainty due to mass measurement	0.0%
4. Uncertainty due to time interval measurement	0.0%
5. Uncertainty due to melt temperature measurement	0.7%
6. Combined expanded uncertainty, U_c^a	12%

a. The combined expanded uncertainty computed by root-sum-of-squares of the component uncertainties was only 11.03%, not statistically distinguishable from the component uncertainty due to reproducibility alone, 11%, considering the uncertainty in reproducibility itself. The combined expanded uncertainty is rounded up to $U_c=12\%$.

SUPPLEMENTAL INFORMATION

The methyl [-CH₃] group content as determined by ASTM Method D2238-68 is 0.15 methyl groups per 100 carbon atoms. This shows the polyethylene to be essentially linear. The differential refractive index in 1-chloronaphthalene, required for the calculation of molecular weight by light scattering, was found to be -0.193 mL/g at 135 °C and 546 nm. The maximum rate of shear in the Ubbelohde viscometer was about 1500 s⁻¹. All measurements were carried out at specific viscosities (0.1 or less) which were sufficiently low for negligible dependence on rate of shear.

Reports describing investigations required for the certification of SRM 1475 (previous lot) are described in references 1-3. A report describing the investigations comparing this current lot, SRM 1475a, with SRM 1475 can be found in reference 4.

REFERENCES

- [1] Hoeve, C.A.J., et al., J. Res. NBS, 76A, 137-170, (1972).
- [2] Chang, S.S., and Bestul, A.B., J. Res. NBS, 77A, 395-405, (1973).
- [3] Chang, S.S., J. Res. NBS, 78A, 387-400, (1974).
- [4] Guttman, C.M. and Maurey, J.R., "Recertification of the SRM 1975a, A Linear Polyethylene Resin," NISTIR 5199, (1993).
- [5] Taylor, B.N. and Kuyatt, C.E., "Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results," NIST Tech. Note 1297, (Jan. 1993).

